NOTE ON AN OBJECTIONABLE METHOD OF FINING WINES.

By R. BODMER.

(*Read at the Meeting, May* 3, 1905.)

About six months ago I was supplied with some Moselle (Zeltinger) by a firm of wine merchants. In several bottles I noticed a blue sediment in the last glass poured out.

I collected some of the sediment and examined it. It proved to be a ferrocyanide of iron, and also gave a distinct reaction for zinc. I was at a loss to understand how these substances could be introduced into wine, but on mentioning the matter to Mr. Hehner he showed me a note in the *Zeitschrift für Untersuchung der Nahrungs und Genussmittel* (1903, p. 452), by Dr. Karl Windisch on certain "finings" which he had examined. They were sold as "Heins Schnell-Klärung," and consisted of two solutions:

1. A solution of zinc sulphate—11·417 grams (cryst.) in 100 c.c.
2. A solution of potassium ferrocyanide—10·52 grams in 100 c.c.

The solutions are supposed to be of exactly equivalent strength.

No. 1 is first added to the wine—about 200 c.c. to 200 litres of wine—and then an equal volume of No. 2. A bulky precipitate of zinc ferrocyanide is formed, which, in settling out, rapidly and completely clarifies the wine.

On further inquiry into the matter, I found that these solutions had actually been used by the importers of the wine under the impression that they contained nothing injurious to health and did not contravene the German wine laws. I may say that this preparation is patented in Germany and Sweden, and is advertised by the vendor as being safe and permissible, and the advertisement contains a certificate from a German analyst to the above effect.

On further examining some of the wine, I detected ferrocyanide in solution after the blue precipitate had been filtered off.

I next obtained some more wine of the same character from a totally different

source. In this I could detect no ferrocyanide in solution nor was there any blue sediment, but the wine contained zinc. In order to corroborate me, Mr. Hehner kindly examined half of a mixture of two bottles of wine, and I examined the other half. Our results agreed very closely. Mr. Hehner found zinc in the proportion of 27·6 mgms. calculated as crystallized zinc sulphate per litre, and I obtained 28 mgms. The latter figure is equivalent to 1·96 grains per gallon, or 0·32 grains per bottle.

Although this proportion of zinc sulphate is small, it is nevertheless decidedly objectionable in a light wine, of which some persons drink as much as two bottles a day.

This process of fining is a most dangerous one. If the solutions do not exactly balance each other, the wine will contain either an excess of zinc sulphate or potassium ferrocyanide.

I have proved by experiment that traces of hydrocyanic acid are evolved from a wine of the acid character of Moselle to which a little ferrocyanide of potassium has been added.

Further, as shown by Dr. Windisch in the note above referred to, zinc ferrocyanide is not entirely insoluble in an acid wine, so that some of the precipitate first formed may be redissolved.

As a warning to wine merchants and importers, a letter signed by Sir Thomas Stevenson, Mr. Hehner, and myself was sent to four wine and spirit trade papers, pointing out the dangerous nature of this preparation.

As to the method of analysis adopted: As a qualitative test, a few drops of ferrocyanide of potassium was added to some of the wine. A bluish-white precipitate was produced, which on further examination was found to contain zinc. This is, of course, not a conclusive test, as some wines which contain no zinc were found to give more or less precipitate with potassium ferrocyanide, no doubt due to the presence of a little albuminous matter in the wine (from isinglass, used as finings). Still, I noted that the quantity of this precipitate was more decided in wine containing zinc than when none was present. For the quantitative determination 500 c.c. of the wine was evaporated, and the residue charred with nitric and sulphuric acid (as in the method for determining arsenic in beer). The residue was well extracted with boiling water and a little hydrochloric acid.

Ammonia was added in excess (after the iron present had been oxidized by boiling with a little nitric acid) and the precipitate of ferric hydroxide, etc., filtered off. The filtrate was acidulated with acetic acid and a stream of SH_2 passed through for some time. The precipitated zinc sulphide, after washing with SH_2 water, was dissolved off the filter with dilute nitric acid and the solution evaporated, ignited, and the residue weighed as ZnO.

In one experiment I ignited the precipitate of ZnS with the filter-paper, and there was a decided loss, owing, no doubt, to reduction of the ZnO to metallic zinc and volatilization. The ignited residue dissolved in dilute HCl gave copious reaction for zinc with ferrocyanide of potassium in acetic acid solution and with ammonium sulphide in ammoniacal solution.

I have been informed by the wine importers from which this wine was obtained

that samples of this identical wine and others in which Mr. Hehner and Dr. Dyer also found zinc were sent to Germany for analysis, and that no zinc was detected in any of them. I ascertained, however, that the wines were incinerated and the ash examined for zinc. Dr. Windisch has pointed out that by this procedure a *loss* of zinc is likely to occur; so this may perhaps account for the fact that the German chemists found no zinc, or else the samples could not have been identical with those examined by Mr. Hehner, Dr. Dyer, and myself.

I have only succeeeded in finding ferrocyanide in solution in one sample—the one first referred to, in which the blue sediment was present, and where the use of these finings was admitted.

A few drops of ferric chloride were added to the wine previously acidulated with a few drops of hydrochloric acid. The blue precipitate—much of which was probably tannate of iron—was filtered off, washed, and boiled with caustic soda solution. The ferric hydrate was filtered off, and the filtrate acidulated with HCl. On adding a drop of ferric chloride a blue precipitate was again obtained.

The mere fact that ferric chloride produces a bluish precipitate with a wine is not conclusive evidence of the presence of a ferrocyanide, as the tannate of iron also has a decidedly bluish tint.

In the paper by Dr. Windisch already referred to he states that "Heins Schnell-Klärung" has been used in Germany to a very considerable extent, and not only for wines but for spirits and liqueurs. I believe, however, that the use of this preparation is now prohibited in Germany, although patented there.